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Phonon-Drag Thermopower in Dilute Copper Alloys

I. Weinberg

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CONTENTS

I. Introduction	1
II. Experimental	2
III. Treatment of Data and Results	3
IV. Calculations and Discussion	5
References	6
Table 1. Residual resistivities, solute concentrations, and values of the scattering parameter for dilute copper alloys	2

FIGURES

1. Thermoelectric power of pure copper	3
2. ΔS, the difference in thermopower between the alloys and pure copper	4
3. ΔS_{ef}, the difference in diffusion thermopower between the alloys and pure copper	4
4. ΔS_{gr}, the difference in phonon-drag thermopower between the alloys and copper	4
5. ΔS_{gr}, the difference in phonon-drag thermopower between Cu + 0.44% Si and pure copper	4

ABSTRACT

N66-22923

The change in phonon-drag thermopower of copper that occurs with alloying is determined for several dilute copper alloys. These results are then used to determine numerical values for the scattering parameter a , assuming pure Rayleigh scattering of phonons by the solute atoms. The values of a obtained experimentally are compared to the scattering parameter calculated for elastic scattering of long-wavelength phonons by the mechanism of mass difference alone. Solute concentrations employed in this investigation are: 0.03 at. % Au, 0.09 and 0.2 at. % Ag, and 0.44 at. % Si. For Cu-Au, the results indicate that phonons are scattered predominantly through the mass-defect mechanism. The Cu-Si data yield a contribution from the mass-defect term that is of the same magnitude as the contribution from other phonon-scattering mechanisms (lattice distortion). For Cu-Ag, the results indicate that phonons are scattered in this alloy predominantly by mechanisms other than mass difference. The relative magnitude of the lattice-distortion contribution is least in Cu-Au, and increases in Cu-Si and Cu-Ag in that order. The Cu-Si data are in agreement with the author's previous results, while for Cu-Ag and Cu-Au, the results are in agreement with qualitative considerations based on the range of solid solubilities in these alloys.

Author

I. INTRODUCTION

Recent theoretical work in the transport properties of metals has resulted, among other things, in a general expression for the phonon-drag thermopower in pure metals (Ref. 1). Using this general expression, Huebener (Ref. 2) has obtained a relation for the change in phonon-drag thermopower due to point defects in a metal. These results have been applied to the attenuation of phonon-drag thermopower due to lattice vacancies in gold (Ref. 2). It is found, on assumption of a pure Rayleigh

law for phonon scattering, that lattice vacancies in gold scatter phonons largely by means of the strain field associated with a vacant lattice site (Ref. 2). If, in the case of alloys, the solute atom may be treated as a point defect, and a pure Rayleigh scattering law is assumed, then the theory developed for lattice vacancies in gold can be applied to the scattering of phonons by solute atoms in dilute alloys. A program of this nature has already been carried out for Cu-Si and Cu-Al alloys (Ref. 3). Using

the theory of Klemens (Ref. 4) to interpret the experimental results, it was concluded that, for Cu-Al, phonon scattering can be attributed largely to the perturbation in mass periodicity caused by the presence of aluminum atoms in the copper host. In Cu-Si, the aforementioned contribution of mass deviation is found to be of the same magnitude as the combined contribution due to a change in force constants and the elastic strain field due to the solute atom (Ref. 3). The current work is an extension of the previous treatment to dilute alloys of gold and silver, respectively, in copper. At the same time, results and analyses are presented for an additional Cu-Si alloy. Attenuation of the phonon-drag component in copper-gold and copper-silver alloys has been previously ob-

served (Ref. 5), complete quenching of the phonon-drag component being noted for 0.96 at. % silver and 0.4 at. % gold, respectively (Ref. 5). In the present work, analysis of phonon-drag attenuation along the lines used in Ref. 3 requires that phonon scattering by impurities be small in comparison to the effects of other phonon-scattering mechanisms. Hence the present solute concentrations are chosen to be markedly lower than those employed by previous investigators (Ref. 5). As in Ref. 3, a major objective of the current work lies in using the change in phonon-drag thermopower that occurs with alloying to obtain information regarding the mechanisms by which solute atoms scatter phonons in dilute copper alloys.

II. EXPERIMENTAL

The sample preparation and experimental techniques are essentially the same as those used in Ref. 3. One difference in the present work lies in the final anneal given all samples. For the current pure copper and alloys, the final vacuum anneal was carried out for 24 hr at a temperature of 600°C, the vacuum being maintained at 10^{-6} torr throughout the annealing operation. The starting materials were ASARCO, 5⁹ purity, copper, silver and gold, while the silicon was Dow-Corning semiconductor grade (6⁹ purity). In all cases the finished product was in the form of 0.010-in.-diam. wire. The annealed pure-copper wires had a resistivity at 4.2°K of $2.09 \times 10^{-3} \mu\Omega \text{ cm}$. Solute content for the alloy wires, as determined by spectrochemical analysis, together with resistivities measured at 4.2°K are listed in Table I. The experimental technique consisted of determining the emf generated by the alloy-copper thermocouple as a function of temperature and differentiating the emf to obtain ΔS , the difference in thermopower between the alloy and copper. Voltages generated by the alloy-copper thermocouples were determined by means of a Rubicon

Table I. Residual resistivities, solute concentrations, and values of the scattering parameter for dilute copper alloys

Solute	Solute, at. %	Resistivity at 4.2°K, $\mu\Omega \text{ cm}$	α from Eq. (4), 10^{-13} sec^3	α_m from Eq. (8), 10^{-13} sec^3
Au	0.03	0.021	1.3	0.93
Ag	0.09	0.017	5.6	0.31
Ag	0.2	0.029	15	0.68
Si	0.44	1.31	2.3	0.96

thermo-free, six-dial potentiometer with a resolution of 0.01 μV . A germanium resistance thermometer was used to determine temperatures from 4.2 to 100°K; for higher temperatures, a copper-constantan thermocouple was used. The temperature measurements are estimated as accurate to 0.1°K.

III. TREATMENT OF DATA AND RESULTS

The method for obtaining ΔS_g , the change in phonon-drag thermopower with alloying, has been detailed previously (Ref. 3 and 5). Hence, for the current alloys, only an outline is presented of the technique used in extracting ΔS_g from the data.

The change in phonon-drag thermopower with alloying is obtained from the relation

$$\Delta S = \Delta S_e + \Delta S_g \quad (1)$$

where ΔS is the experimentally measured difference in thermopower between the alloy and pure copper, and ΔS_e , the computed difference in diffusion thermopower, is given by

$$\Delta S_e = \frac{S_e^{Cu}}{(W_e^0/W_e^1) + 1} \left[\frac{S_e^1}{S_e^{Cu}} - 1 \right] \quad (2)$$

where S_e^{Cu} is the diffusion thermopower of pure copper, W_e^1 is the electronic thermal resistivity due to the solute, and W_e^0 is the intrinsic electronic thermal resistivity of copper. The quantity S_e^1 is the characteristic thermopower of the solute in copper. The diffusion thermopower S_e^{Cu} is obtained from the Kohler equation (Ref. 6)

$$S_e^{Cu} = \frac{\sum_i W_e^i S_e^i}{\sum_i W_e^i} \quad (3)$$

where W_e^i and S_e^i are the electronic thermal resistivity and characteristic thermopower due to the i th scattering agent in copper. In obtaining S_e^{Cu} from Eq. (3) the effects of trace amounts of iron, which cause a large negative peak at low temperatures, are taken into account, using the data of Gold et al. (Ref. 7). Figure 1 shows the measured thermopower of the pure copper, together with S_e^{Cu} , the diffusion thermopower computed from Eq. (3). The difference between the two curves of Fig. 1 yields S_g^{Cu} , the phonon-drag thermopower of copper. The absolute thermopower of copper was obtained by measuring ΔS for a copper-lead thermocouple, then using the values given by Christian et al. for the thermopower of lead

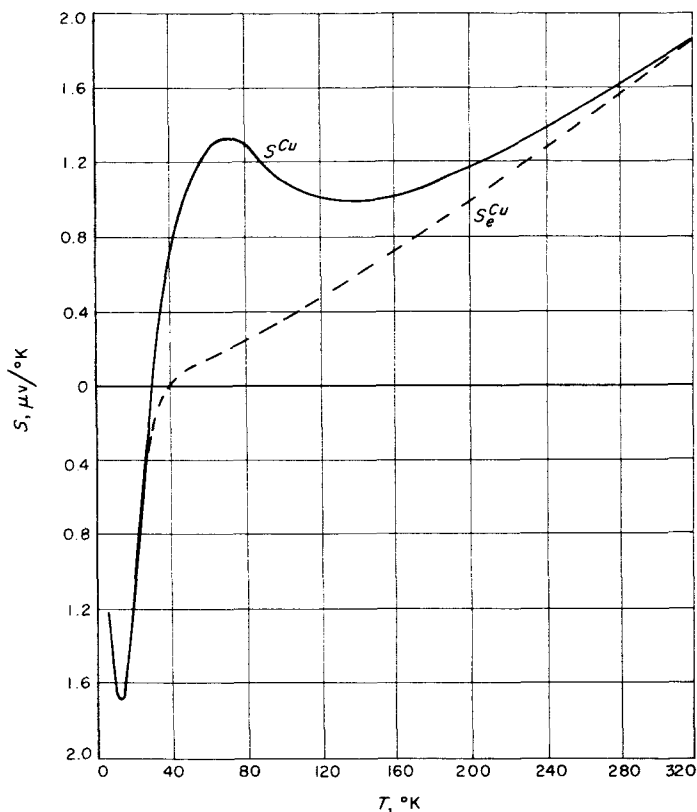


Fig. 1. Thermoelectric power of pure copper

(Ref. 8). In accordance with previous assumptions (Ref. 3 and 5), the phonon-drag thermopower of copper is assumed to be negligible at 320°K. The measured change in thermopower for the copper-alloy thermocouples is shown in Fig. 2. The present work is concerned solely with the phonon-drag component for $T > 80^\circ\text{K}$, hence the alloy data are taken only over the temperature range from $T = 78$ to 320°K. On the other hand, in order to account for the effects of iron (Ref. 7), the pure-copper data must be taken from 4.2 to 320°K. Figure 3 shows ΔS_e for the alloys as computed from Eq. (2) and (3). In Eq. (2) it is assumed that S_e^1 is proportional to temperature, hence determination of S_e^1 at 320°K is sufficient to determine this quantity over the entire range of temperatures (Ref. 5). Returning to Fig. 3, it is noted that ΔS_e for Cu-Ag and Cu-Au is small, which is in agreement with previous results for higher concentrations (Ref. 5). In the Cu-Si alloy, the valence difference between solute and solvent is reflected in the relatively large value obtained for ΔS_e (Ref. 3). Figures 4 and 5 illustrate ΔS_g , the difference in phonon-drag thermopower.

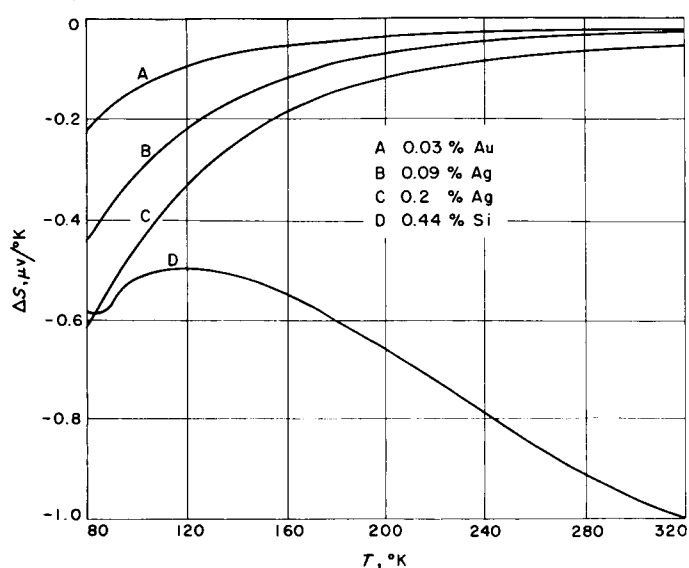


Fig. 2. ΔS , the difference in thermopower between the alloys and pure copper

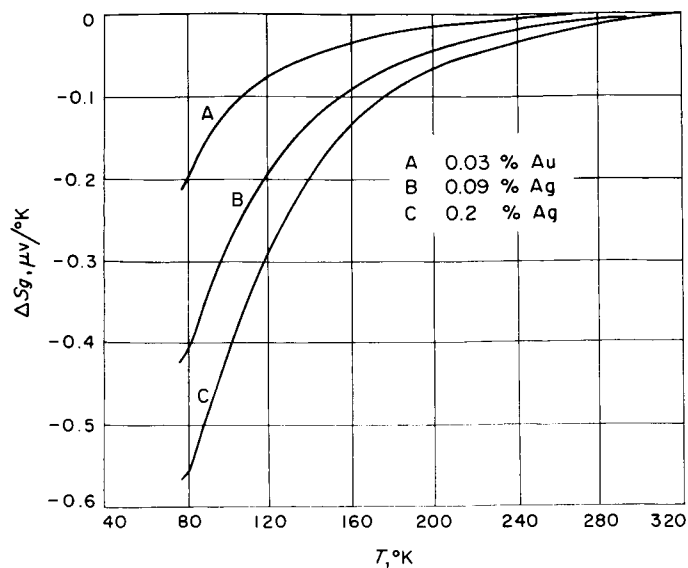


Fig. 4. ΔS_{gr} , the difference in phonon-drag thermopower between the alloys and copper

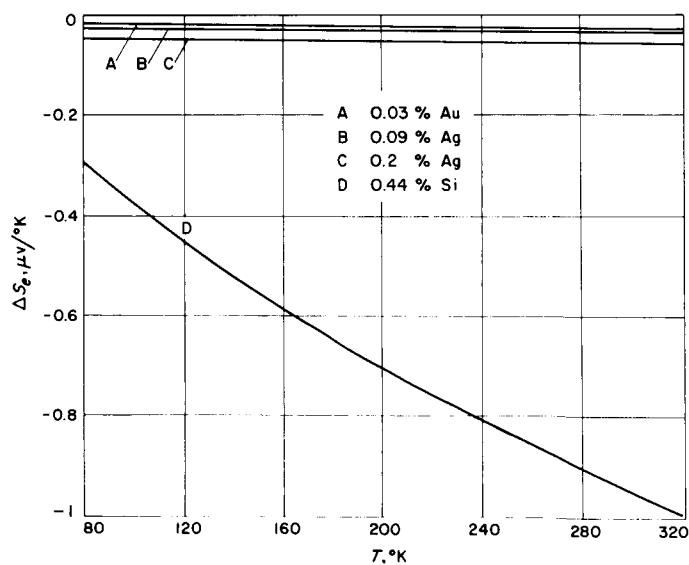


Fig. 3. ΔS_{er} , the difference in diffusion thermopower between the alloys and pure copper

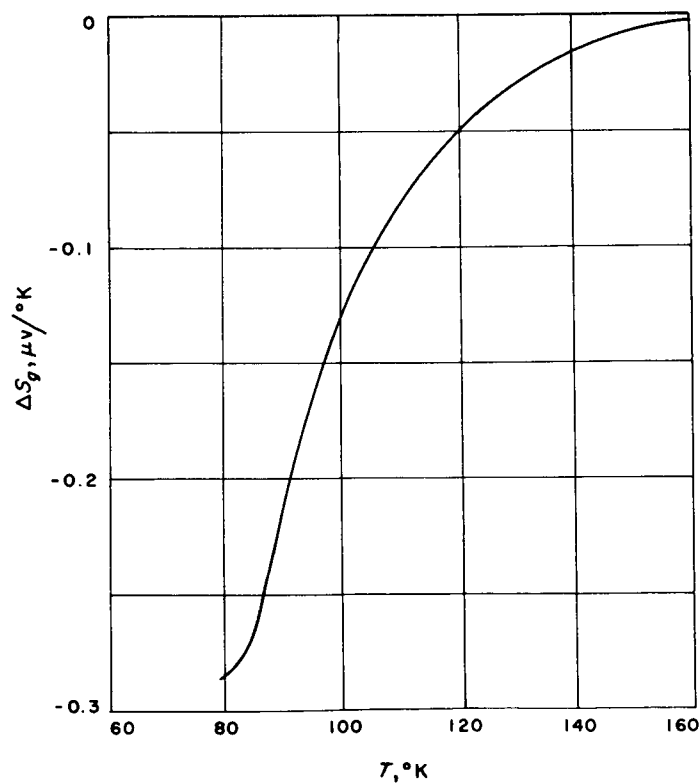


Fig. 5. ΔS_{gr} , the difference in phonon-drag thermopower between Cu + 0.44% Si and pure copper

IV. CALCULATIONS AND DISCUSSION

At temperatures where phonon-phonon collisions dominate in the pure metal (Ref. 2),

$$\Delta S_g = -A e^{\beta/T} \int_0^{\theta/T} \frac{Z^2 e^Z dZ}{(e^Z - 1)^2 \left[1 + \frac{b \hbar^2 e^{-\beta/T}}{a k^2 Z^2 T} \right]} \quad (4)$$

where $Z = \hbar\omega/kT$ (ω being the phonon frequency), \hbar is the Planck constant divided by 2π , θ is the Debye temperature, and A , β , a , and b are constants. It is assumed, in obtaining Eq. (4), that τ_i , the relaxation time for phonon-impurity scattering in the alloy, and τ_0 , the relaxation time for phonon-phonon scattering in the pure metal, are of the form (Ref. 2)

$$\tau_i^{-1} = a\omega^4 \quad (5)$$

$$\tau_0^{-1} = b\omega^2 T e^{-\beta/T} \quad (6)$$

The ω^4 dependency for τ_i^{-1} follows from the assumption of pure Rayleigh scattering (Ref. 2 and 4). The relaxation time τ_0 is essentially empirical and has been chosen to fit lattice thermal conductivity data (Ref. 2, 3, and 9).

An objective of the present work is the evaluation of a , using Eq. (4). This can be accomplished by numerical integration provided that A , β , and b are known. The constants b and β have already been evaluated in Ref. 3 from the lattice thermal conductivity of pure copper. The values obtained are $b = 4.19 \times 10^{-18}$ sec deg⁻¹ and $\beta = 43.6^\circ\text{K}$. The constant A is evaluated from the expression (Ref. 2)

$$S_g^{cu} \approx A e^{\beta/T} \int_0^{\theta/T} \frac{Z^2 e^Z dZ}{(e^Z - 1)^2} \quad (7)$$

Using the value of S_g^{cu} at $T = 90^\circ\text{K}$ (from Fig. 1) with $\theta = 310^\circ\text{K}$ (Ref. 10), it is found that $A = 0.21 \mu\text{V}/^\circ\text{K}$. The parameter a may now be evaluated from Eq. (4) by numerical integration, using an IBM 7090 computer. The results are shown in Table 1.

Consideration of elastic phonon scattering by point defects in the long-wavelength limit leads to theoretical relations for τ_i of the form given in Eq. (5) (Ref. 4 and 11). The assumption of elastic scattering is restric-

tive in the sense that inelastic scattering leads to deviations from a pure Rayleigh scattering law (Ref. 12 and 13). For the present case, a Debye spectrum is assumed (Ref. 2) in the theory leading to Eq. (4). Furthermore, it is assumed that the phonon spectrum is unchanged by alloying (Ref. 2). Consistent with these assumptions, the Klemens theory (Ref. 4) was used to calculate the scattering parameter for comparison with the current experimental values. Using the Klemens theory, it is a relatively simple matter to calculate a for scattering of phonons by a substitutional impurity differing only in mass from the atoms of the host crystal. In addition, the theory contains terms due to changes in force constants and the strain field associated with a point defect. However, the calculations for phonon-scattering mechanisms, other than mass difference, are relatively inexact. This is due partly to approximations in the Klemens theory and partly, in the case of metals, to the difficulties associated with computing interatomic force constants (Ref. 14). Hence only the mass-difference mechanism is considered in the present calculation. The scattering parameter calculated in this way is designated by the symbol a_m . Thus (Ref. 4)

$$a_m = \frac{\Omega f}{4\pi v_s^3} \left[\frac{\Delta M}{M} \right]^2 \quad (8)$$

where Ω is the atomic volume, f is the fraction of solute atoms present in the metal, v_s is the velocity of sound, M is the average mass for the atoms of the host crystal, and ΔM is the difference in mass between the solute atoms and copper. The values calculated for a_m from Eq. (8) are shown in Table 1. In obtaining these results the value used for v_s was 2.37×10^5 cm sec⁻¹ (Ref. 3).

The mass-defect term in Cu-Au lies reasonably close to the experimental value, while for Cu-Ag a considerable discrepancy exists. Comparing the calculated mass-defect term with the experimental value, the relative contribution from lattice distortion¹ is lowest in Cu-Au, and increases in Cu-Si and Cu-Ag in that order. The present copper-silicon results indicate a contribution from lattice distortion that is of the same magnitude as the mass-defect term, which is in agreement with previous conclusions

¹The term "lattice distortion" includes the effects of a change in force constants together with the effects of the elastic strain field due to the solute atoms. The terminology used here conforms to that used in Ref. 4 and 15.

based on thermoelectric power (Ref. 3) and lattice thermal conductivity (Ref. 15). For copper-gold, results from lattice thermal conductivity (Ref. 15) indicate that phonons are scattered in this alloy predominantly through the mass-defect mechanism, a conclusion supported by the results of the current investigation. The Cu-Ag results indicate that in this alloy the contribution from lattice distortion is predominant. In this respect, it is of interest to compare the results for the gold and silver alloys. The wide range of solid solubility for gold in

copper (Ref. 16) indicates that in this alloy the solute atoms should not unduly disturb the host lattice. Hence one should be able to calculate the phonon-scattering probability reasonably well by considering only mass difference. On the other hand, the solubility of silver in copper is rather limited (Ref. 16) and the $(\Delta M/M)^2$ term is much less than that for copper-gold. From these considerations, a much larger relative contribution would be expected from lattice distortion in Cu-Ag as compared to Cu-Au. This is in agreement with the present results.

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